［物理化学標準］

以下の問（1），（2）に答えよ．

（1）下式の逐次１分子反応に従って，反応物 **R** は中間体 **I** を経て生成物 **P** へと変換される．

$$\mathbf{R} \xrightarrow{k_1} \mathbf{I} \xrightarrow{k_2} \mathbf{P}$$

ここで，k_1 と k_2 は各素過程の速度定数を，括弧[ ]は化学種の濃度を表す．ただし，$k_1 \neq k_2$ とする．

(a) 反応時間 t に対して，[**R**], [**I**], [**P**]の微分反応速度式をそれぞれ記せ．

(b) **R, I, P** の初期濃度がそれぞれ $[\mathbf{R}]_0, 0, 0$ のとき，[**R**]を t の関数として表せ．

(c) [**I**]が下式で与えられるとき，係数 α_1 と α_2 を$[\mathbf{R}]_0$，k_1，k_2 を使って表せ．

$$[\mathbf{I}] = \alpha_1 \exp(-k_1 t) + \alpha_2 \exp(-k_2 t).$$

(d) (c)で与えられた[**I**]が最大値を取る反応時間 t_{max} を k_1，k_2 を使って表せ．

(e) [**I**]に対して定常状態近似が適用できるときの濃度 $[\mathbf{I}]_{ST}$ を，問(a)の微分速度方程式を用いて t の関数として表せ．

(f) [**I**]が$[\mathbf{I}]_{ST}$で近似できるための条件を二つ示せ．また，各々の条件の物理的な意味を簡潔に述べよ．

（2）

(g) 光吸収によって電子的に励起された分子は，蛍光などの様々な緩和過程を経て基底状態にもどる．無放射遷移の名称を二つあげ，それぞれの過程で励起分子がどのように緩和されているか説明せよ．

(h) ある色素分子の電子励起状態の寿命（τ）が 4.0 ns で，蛍光量子収率（Φ_f）が 0.80 のとき，蛍光寿命 τ_f および無放射遷移の寿命 τ_{nr} を有効数字２桁で求めよ．

(i) Xe と HCl の混合気体を放電して生成した励起錯体 XeCl*は波長 308 nm の光を発する．XeCl の電子基底状態と電子励起状態の模式的なポテンシャル曲線を描き，なぜこの光学遷移がレーザー発振に適しているのか，その理由を説明せよ．

[Physical Chemistry: Standard]

Answer problems (1) and (2).

(1) Product **P** is produced from reactant **R** via intermediate **I** according to the following consecutive unimolecular reaction:

$$\mathbf{R} \xrightarrow{k_1} \mathbf{I} \xrightarrow{k_2} \mathbf{P},$$

where k_1 and k_2 are the rate constants of the individual elementary steps. The square brackets [ ] indicate the concentrations of chemical species inside the brackets. Here assume $k_1 \neq k_2$.

(a) Express differential rate equations for [**R**], [**I**], and [**P**], respectively, with respect to reaction time t.

(b) Express [**R**] as a function of t if the initial concentrations of **R**, **I**, and **P** are given by $[\mathbf{R}]_0$, 0 and 0, respectively.

(c) Express α_1 and α_2 in terms of $[\mathbf{R}]_0$, k_1, and k_2 by assuming [**I**] as follows:
$[\mathbf{I}] = \alpha_1 \exp(-k_1 t) + \alpha_2 \exp(-k_2 t)$.

(d) Using [**I**] given in problem (c), find $t = t_{max}$ that maximizes [**I**] in terms of k_1 and k_2.

(e) $[\mathbf{I}]_{ST}$ represents the concentration of **I** in the steady state if the steady-state approximation is applicable. Express $[\mathbf{I}]_{ST}$ as a function of t using the differential rate equation in problem (a).

(f) List two conditions where [**I**] can be approximated to $[\mathbf{I}]_{ST}$. Briefly explain the physical meaning of each condition.

(2)

(g) A molecule excited into an electronically excited state by photoabsorption undergoes a number of relaxation processes including fluorescence. List two nonradiative transitions and explain how the excited molecule is relaxed in these processes.

(h) A certain dye molecule has the lifetime of the electronically excited state (τ) of 4.0 ns and the fluorescence quantum yield (Φ_f) of 0.80. Calculate the lifetimes of fluorescence (τ_f) and nonradiative transitions (τ_{nr}) to two significant figures.

(i) Excited complex XeCl* produced by the discharge of a gas mixture of Xe and HCl emits a 308 nm photon. Draw schematic potential curves of XeCl in the electronically ground and excited states and explain why this optical transition is suitable for laser emission.